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INVESTIGATION OF SOLUBILITY AND DIFFUSION OF OXYGEN IN REFRACTORY METALS

FIRST QUARTERLY REPORT

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS 3-7626

A DIVISION OF VARIAN ASSOCIATES

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ABSTRACT

Electrical resistivity measurements will be used to determine the solubility limits and diffusion constants of oxygen in tantalum, Ta-10W, alloy T222, columbium, Cb-1Zr, and alloy FS-85.

An oxygen solubility determination apparatus has been designed and constructed.

An analysis of the literature is in progress.

I. INTRODUCTION

This investigation concerns oxygen diffusion and solubility in commercially pure refractory metals and in advanced alloys for space power system components Oxygen contamination of refractory metals reduces their resistance to alkali metal corrosion. Accurate knowledge of oxygen diffusion constants and solubility limits are required in order to establish realistic engineering and environmental specifications.

This investigation is divided into two phases:

Phase I. A determination of the limits of oxygen solubility in commercially pure tantalum and columbium and in the alloys Cb-1Zr, Ta-10W, FS-85 (Cb-28Ta-10.5W - 0.9Zr), and T222 (Ta-9.8W-2.4Hf-0.01C), at five temperatures in the temperature range of 1000°F to 2400°F.

Phase II. The determination of average diffusion constants of oxygen in the materials listed above across four different concentration couples and at four temperatures in the range of 1600°F to 2400°F.

Solubility limits and diffusion constants will be determined from electrical resistivity data using commercially obtainable wires for specimen samples. Absolute oxygen contents shall be determined by neutron activation analysis. Other methods of analysis such as electron microprobe analysis, X-ray diffraction analysis, microhardness and conventional chemical analysis will be

employed for obtaining corroborating data.

It is expected that the data obtained on the pure metals will confirm the previously reported data in the literature and provide the required confidence level to pursue alloy solubility data.

II. SUMMARY

During this first quarter the major activity was the design and construction of a solubility determination apparatus. This consists of an electronic feedback controlled 1000°C vacuum furnace with an oxygen feed system and means for precise measurement of electrical resistivity and temperature of the sample.

A literature search and review was initiated. Of specific interest is the literature reporting work on oxidation and oxygen reaction rates of the materials with which this program is concerned.

Wires of Cb and Ta were obtained and a trial solubility run was made to prove out the apparatus. All systems were found to function satisfactorily with the exception of a defective valve and coupling which were not vacuum tight.

III. PRIOR INVESTIGATION

A. Some Previous Work on Oxygen Solubility

Many physical properties have been utilized to determine oxygen solubility in the refractory metals; some of which can be employed to corroborate the findings of the resistivity measurements.

Seybolt[3] used a Sieverts' apparatus to introduce a known amount of oxygen into a fused silica vacuum furnace tube in which was hung a columbium strip 0.02 x 0.5 x 2.0 in. For alloys containing more than 0.75% O_2, he used a bulk oxidation and diffusion process employing arc melted mixtures of Cb and Cb_2O_5. These mixtures were arc melted and diffusion homogenized for 24 hours at temperatures in the region 800°C - 1100°C to obtain the equilibrium amount of oxygen dissolved in Cb in equilibrium with CbO. Using an X-ray technique, lattice parameters were determined as a function of the oxygen content as determined from the Sieverts runs. His results were compared with the equilibrium lattice parameter values obtained from the arc cast specimens. The solubility of oxygen was found to vary from 0.25% at 775°C to 1.0% at 1100°C. The 1100°C value is higher than that reported by Elliot[4], (0.4%) whose data is used by English[5] to construct the Cb-O phase diagram. Elliot used a series of master alloys similar to Seybolt. Gebhardt and Rotherbacher's data[6] agree very well with Seybolt at the lower

temperature but again a difference is noted at the higher temperatures, (0.5% at 1100°C). The latter authors used micro-hardness and electrical conductivity data to supplement their lattice parameter data[6]. Gebhardt and co-workers had previously used these same techniques to establish the solubility of oxygen in tantalum[7]. Oxygen charges introduced at a pressure of 2×10^{-2} torr were step-wise reacted with the columbium after the 0.030 x 5.3 in. wire had been outgassed at 2500°C at 5×10^{-6} torr by passing current through the wire. A lower oxide of Ta than Ta_2O was found, namely Ta_4O. No great preponderance of reliable solubility data on the alloys treated in this program has been found in the literature.

3. Rate Controlling Processes

Oxygen is reacted and absorbed into refractory metals in four distinct steps:

1. Bombardment of surface
2. Physical adsorption
3. Chemical absorption
4. Diffusion into bulk of material

In the case of tantalum the diffusion process appears to be slower than the chemisorption at pressures in the region of 1×10^{-2} torr and above as, subsequently, a finite time under high vacuum conditions is necessary for the electrical resistivity value to attain equilibrium after exposure to a charge of oxygen.

At lower partial pressures of oxygen, it is expected that chemisorption will be the rate controlling factor. In the case of columbium, Gebhardt and Rothenbacher[9] indicate that chemisorption is the controlling factor over the pressure range 10^{-3} torr to 10^{-5} torr in the temperature range 0 to 1000°C.

Possible difficulties are anticipated involving the formation of CbO_2 which can be expected to have a detrimental effect on the resistivity measurements and is not as easily taken into solution as CbO. It may be necessary to engas columbium and columbium alloys at very low pressures ($< 10^{-5}$ torr)[8] to encourage the formation of CbO at the surface in preference to CbO_2 and to eliminate scaling problems encountered at higher pressures.

IV. EXPERIMENTAL PROCEDURES

A. Selected Technique for Solubility Determination

Several procedures for oxygen determination from resistivity measurements have been considered in detail.

Technique 1. Crossing the oxygen solubility curve isothermally by reaction with known amounts of oxygen

Technique 2. Measuring resistivity as a function of decreasing and then increasing temperature with total oxygen content as a constant.

In both cases direct heating and indirect heating of the sample were considered

The experimental procedures to be followed were selected primarily because of expected greater accuracy.

The selected procedure 2) employs a reaction tube heated by a furnace with thermocouple feedback to a controller which varies the power available to the furnace. The specimen wire is to be heated in vacuum to a temperature level above the estimated solubility curve and then charged with a known amount of oxygen. (The exact oxygen content shall be determined, to ± 10 ppm, after each run, by neutron activation analysis) Resistivity shall be measured at temperature. The temperature will be reduced stepwise in order to straddle the oxygen solubility line of the appropriate phase diagram (see Figure 1) These temperatures and the corresponding resistivities will be recorded.

While the absolute resistance increases at constant temperature with oxygen engassing, in the near vicinity of, but above, the solubility line (Region A) the slope of resistivity versus temperature will reflect the temperature coefficient of resistivity for the oxygen free material. In the near vicinity of, but below, the solubility line, Region B, the slope of resistivity versus temperature will be a linear function of both the temperature coefficient of resistivity of the metallic phase and the temperature coefficient of resistivity of the precipitated oxide phase[2]. (Care will be taken to maintain a constant cooling rate). The two slopes will intersect at temperature T_s where T_s represents the temperature at which the oxide phase will first precipitate. Sufficient runs will be made to determine the oxygen solubility limits within the temperature range 1000°F to 2400°F with the further restriction that the maximum oxygen content investigated will be limited to 10,000 ppm (1%).

B Definition of Solubility

In the case of the specific alloys to be investigated (Cb-1Zr, Ta-10W, FS-85, T222), the meaning of oxygen solubility limit is somewhat arbitrary. For instance, in the case of the Cb-1Zr alloy the first oxide phase to precipitate under equilibrium conditions will be ZrO_2 and in the case of alloy T222, CO volatilization can be expected to occur. (It may not be possible to attain equilibrium within a realistic time interval at the lower temperatures (1000°F). Detailed hypothetical pseudo-equilibrium phase diagrams of the various reaction paths that can occur

in these systems have been prepared and will be presented in subsequent reports along with the experimental data obtained for these systems.

It should be noted that the concept of a "pseudo-solubility" may well have to be invoked in order to develop realistic engineering design data.

V. APPARTUS

A. Apparatus for Oxygen Solubility Determination

An oxygen solubility determination apparatus has been constructed (see Figure 3). This is a preliminary apparatus which will be employed to obtain initial data in the temperature range to 1000°C. (A full temperature range dual vacuum furnace capable of 1500°C is being designed and constructed and will supplement the present 1000°C furnace).

The preliminary solubility apparatus consists of an Oxygen Feed System; a dry vacuum system; the 1000°C furnace with feedback control; a Resistivity and Temperature Measurement System; and a "Dutchman" (vacuum manifold).

A.1 Oxygen Feed System

The oxygen feed system must supply various amounts of gas at variable rates as dictated by the conditions of each experimental run. There are six test materials involved and the data is to be collected at five different temperature levels. The requirements for some of these materials is predictable but oxygen solubility data is sufficiently meagre on the alloys to necessitate designing considerable flexibility into the system[8].

The oxygen feed system to be used in the initial experimental runs is shown schematically in Figure 4. Gas can be fed into the "Dutchman" either in discrete charges or

continuously. Discrete charges can be supplied by trapping gas at tank pressure between valves V3 and V4 and evacuating the balance of the system. The trapped gas may then be fed into the "Dutchman" through VL or MV. Alternatively, gas may be trapped at lower pressures (10^{-6} torr to 1 torr) and fed directly through V4. Continous gas feed over a wide range of flow rates can be accomplished directly by use of VL or MV. Feed pressure can be monitored by the Millitorr gage (high pressure nude ionization gage, 10^{-6} torr to 1 torr). The continuous feed rate shall be calibrated, as required, by means of the 1 liter/sec orifice in the high vacuum manifold.

All valves in the feed system are bakeable to 400°C. All tubing is stainless steel and connections are made with Swage-locks. It is not anticipated that the oxygen feed system shall be expected to meter precise amounts of oxygen to the hot furnace reaction tube containing the wire sample. Since some of the oxygen would be adsorbed on the walls of the furnace tube it is proposed to rely on neutron activation to determine the amount of oxygen in the sample instead. Should it become desirable to measure the oxygen supplied to a greater degree of accuracy the apparatus can be modified to do so.

The oxygen supply shall consist of a cylinder of research grade oxygen and a two stage "anti-diffusion" regulator.

The oxygen feed system as described herein has been built and installed in the preliminary solubility apparatus.

A.2 Vacuum System

The vacuum system (see Figure 3) employs a sorption pump for rough pumping; a forty liter/sec ion pump; and controller for attaining high vacuum. A one liter/sec orifice is located above the ion pump; a bypass arm and bypass valve are provided. A Bayard-Alpert ionization gage measures pressure between the orifice and an isolation valve adjacent to the "Dutchman". A C.E.C. 21-612 Residual Gas Analyzer (modified) is also mounted in this vicinity. The high vacuum part of this system is bakeable to 450°C.

A.3 1000°C Furnace

The 1000°C furnace (see Figure 3) consists of a resistance heated air furnace surrounding a fused quartz reaction tube . The furnace is 13 inches long and is mounted on tracks while the quartz tube is stationary. Furnace temperature profile is shown in Figure 2.

A.4 The "Dutchman"

The "Dutchman" (see Figure 3) is the vacuum manifold adjacent to the furnace tube. It joins the vacuum system, the oxygen feed system and the reaction tube.

Its top flange has two high-current feed-throughs; an octal electrical feed-through; and an octal Pt-Pt 10 % Rh thermocouple feed-through. The wire sample is supported by molybdenum rods attached to the vacuum side of the high-current feed-throughs. The sample wire is lowered into the reaction tube by lowering this top flange into position.

A.5 Temperature and Resistance Measurement Apparatus.

Resistivity shall be determined at temperature by means of a Kelvin Bridge. The bridge is made up of a Leeds & Northrup #4300 Adjustable Standard, #4320 Ratio Box, and #2430-C Galvanometer.

The sample wire is connected to 0.500 dia. high-current high-vacuum copper feed throughs and to potential leads located within the area of uniform sample temperature. The sample wire thus connected constitutes a four terminal resistor.

Temperature measurements on the sample will be taken with Pt- Pt 10 Rh thermocouples, and a Leeds & Northrup Model K-3 potentiometer. There is provision on the thermocouple vacuum feed-through for four pairs of Pt-Pt 10 Rh leads. The furnace monitor thermocouple emf is recorded on an L & N recorder which provides a graphic record of the furnace temperature. A proportional signal is fed to

the furnace control unit which maintains temperature to $\pm$ .5°C.

B. Sample Geometry

The selection of sample geometry for solubility studies was dictated by several considerations:

a) Sample to have maximum surface to volume ratio to facilitate reaching equilibrium quickly.

b) Sample mass to be greater than 1 gram but not more than 5 grams as required for neutron activation analysis.

c) Sample resistance to be $\gg$ 1 ohm (Wheatstone Bridge) or $\ll$ 1 ohm (Kelvin Bridge).

d) Sample geometry selected must be readily available in all six test materials.

Wire 0.020 in. in diameter was chosen as the best compromise between these factors. While a single strand of wire presents the minimum surface to volume ratio (a), this is not too serious for wire as thin as 0.020. Further, surface area can be increased by employing several strands in parallel. Judicious choice of number of strands and wire length will optimize sample mass (b) and sample resistance (c).

C. "Hot Wall" vs. "Cold Wall" Reaction Tube

The "hot wall reaction tube" furnace concept as opposed to a "cold wall reaction tube" wherein the sample is self heated by

passing a current through it, was chosen because of the stringent temperature control requirements ($\pm$ 2°C).

A proven feedback controlled furnace power supply system for a "hot wall reaction tube" furnace was available whereas a preliminary design study of self heating systems was not promising. Among the difficulties to be expected with self-heating is that of maintaining constant temperature (within $\pm$ 5°C) over the sample length. Local variations in resistance, due to variations in wire diameter, for instance, cause variations in temperature which, as engassing ensures, cause even greater local differences in temperature.

The chief drawback to the "hot wall" concept is the engassing and degassing of the hot reaction tube. This is to be minimized by employing good vacuum practices; by maintaining a high vacuum during temperature and resistivity measurements (10^{-6} torr), and by employing neutron activation analysis to determine actual total oxygen content.

It is to be noted however that there is no inherent limitation in the present design that would preclude adopting the "cold wall" self heating mode of operation should this be found necessary.

One variation of procedure that can be tried is to engas the wire sample using the self heating approach and then to homogenize and make measurements using the "hot wall" approach.

Further, if the proposed 1500°C furnace is a high vacuum furnace, as the initial plan contemplates (see IV), the reaction tube could be eliminated when using this latter, modified procedure.

VI. RESULTS

A. Equipment Prove-in

A trial run with the initial solubility apparatus (1000°C air furnace) was concluded in the latter part of this quarter. All systems functioned satisfactorily with the exception of the oxygen feed system.

A valve and coupling were found to have small leaks so that the base pressure in the oxygen feed system was about 10^{-5} torr.

The vacuum system was given a low temperature bake out overnight and a base pressure of about 2×10^{-8} was achieved.

Difficulty was encountered in positioning the sample within the confines of the present 3/4" diamter quartz reaction tube. There are at least six wires in close proximity (two current leads, two potential leads, and two leads for each thermocouple) which must not make contact with each other. The problem was alleviated by the use of quartz insulators.

VII. DISCUSSION

Experimental Technique 1 (see section IV A) is a proven and reliable method of obtaining solubility data.

Technique 2 (see section IV A) is unproven but if it can be used successfully, it will minimize experimental complexity. However, metallurgical phase changes to be encountered, typically exhibit delayed precipitation from solution or frozen-in initial states. If this occurs in the present instance, Technique 1 will be programed.

VIII. CONCLUSIONS

While experimental results preclude extensive conclusions, the following points may be made:

1. The term "oxygen solubility" is somewhat arbitrary with regard to the alloys.
2. Data reported in the literature for oxygen solubility in Ta and Cb is conflicting and of limited accuracy.

IX. PROGRAM FOR NEXT QUARTER

1. Design and construction of a double vacuum 1500°C furnace to supplement the 1000°C air furnace.
2. Design of diffusion study apparatus.
3. Certification of complete solubility apparatus.
4. O_2 solubility determination for Ta and Cb.

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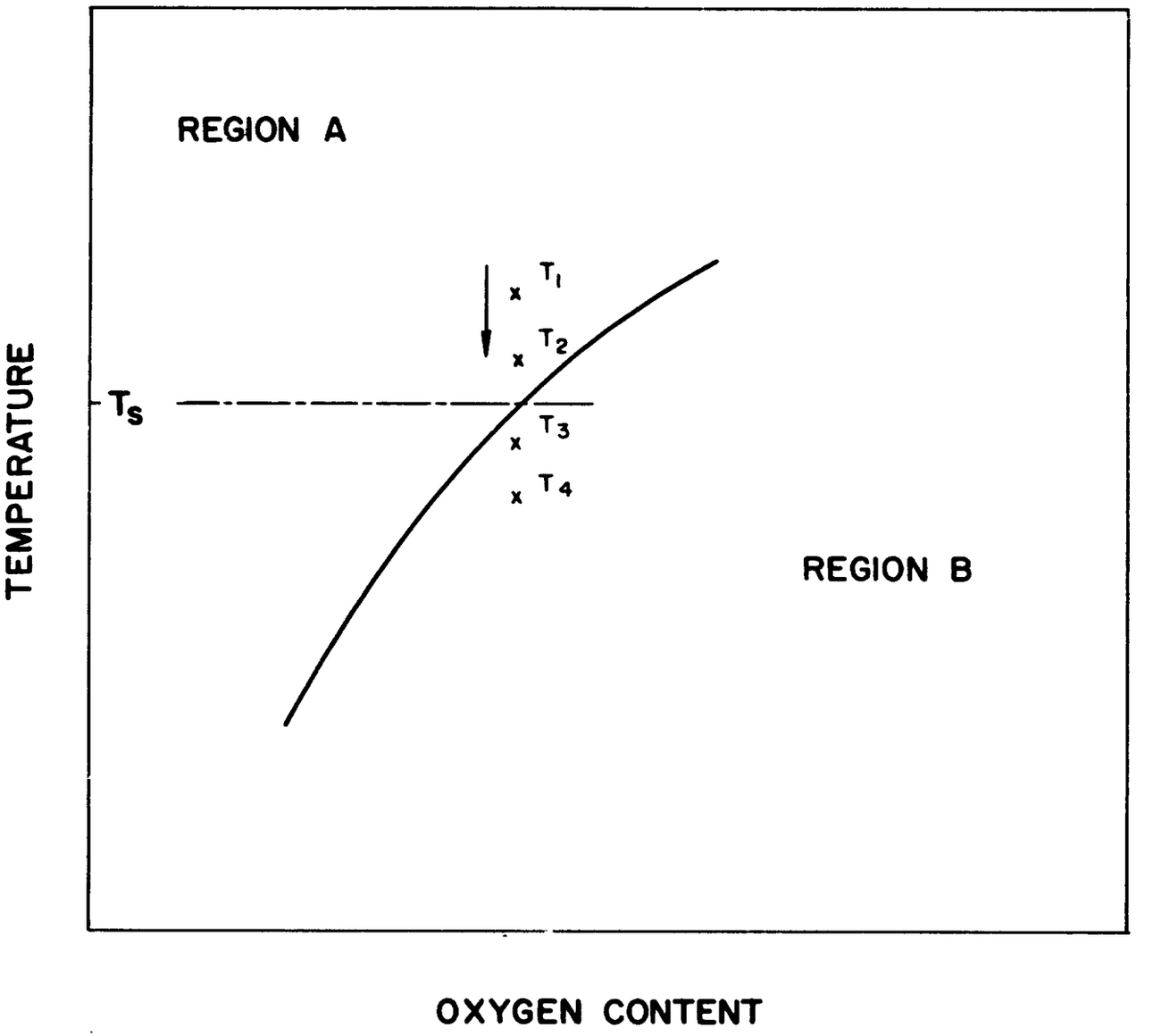


Fig.I OXYGEN SOLUBILITY CURVE

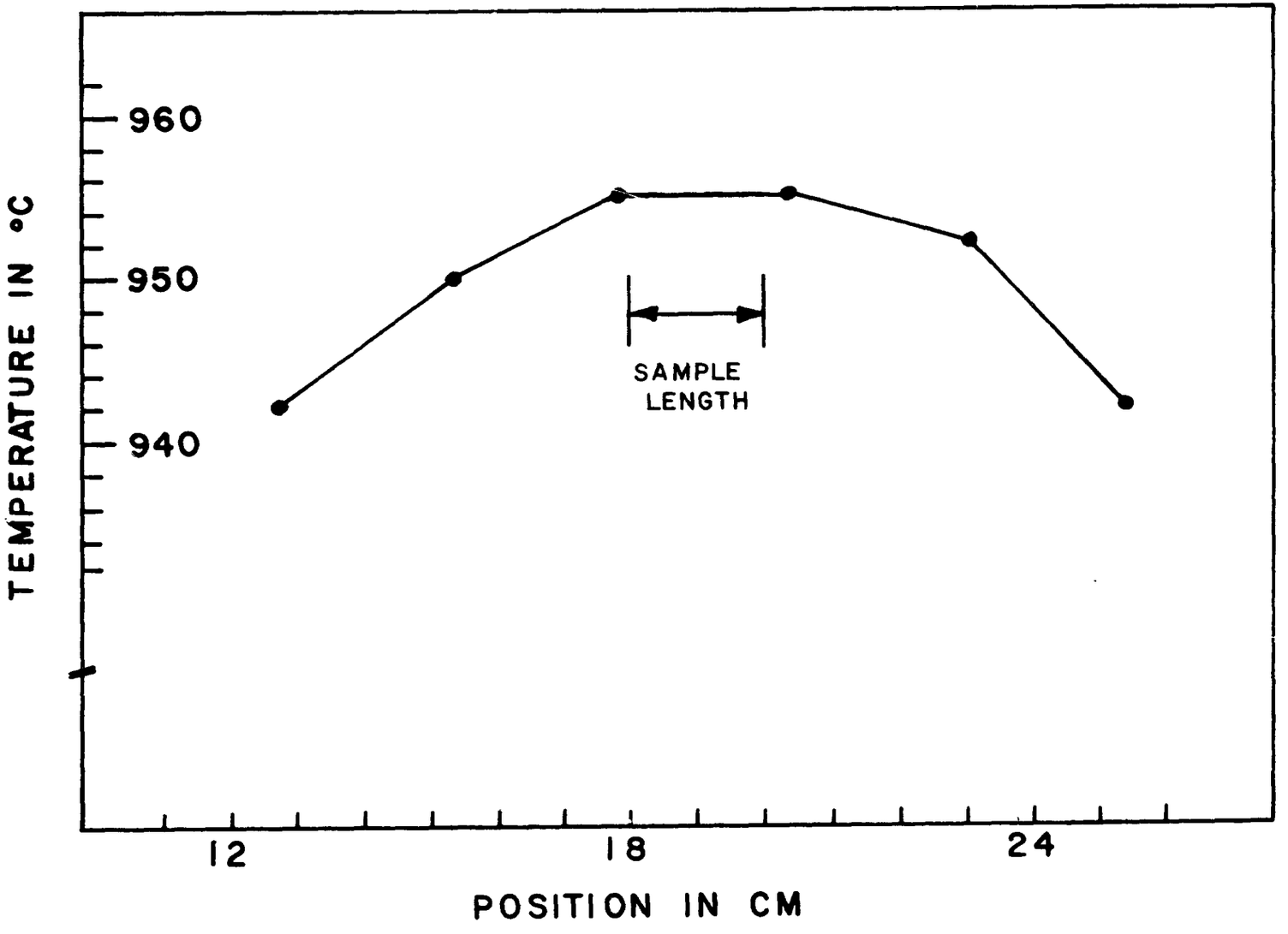
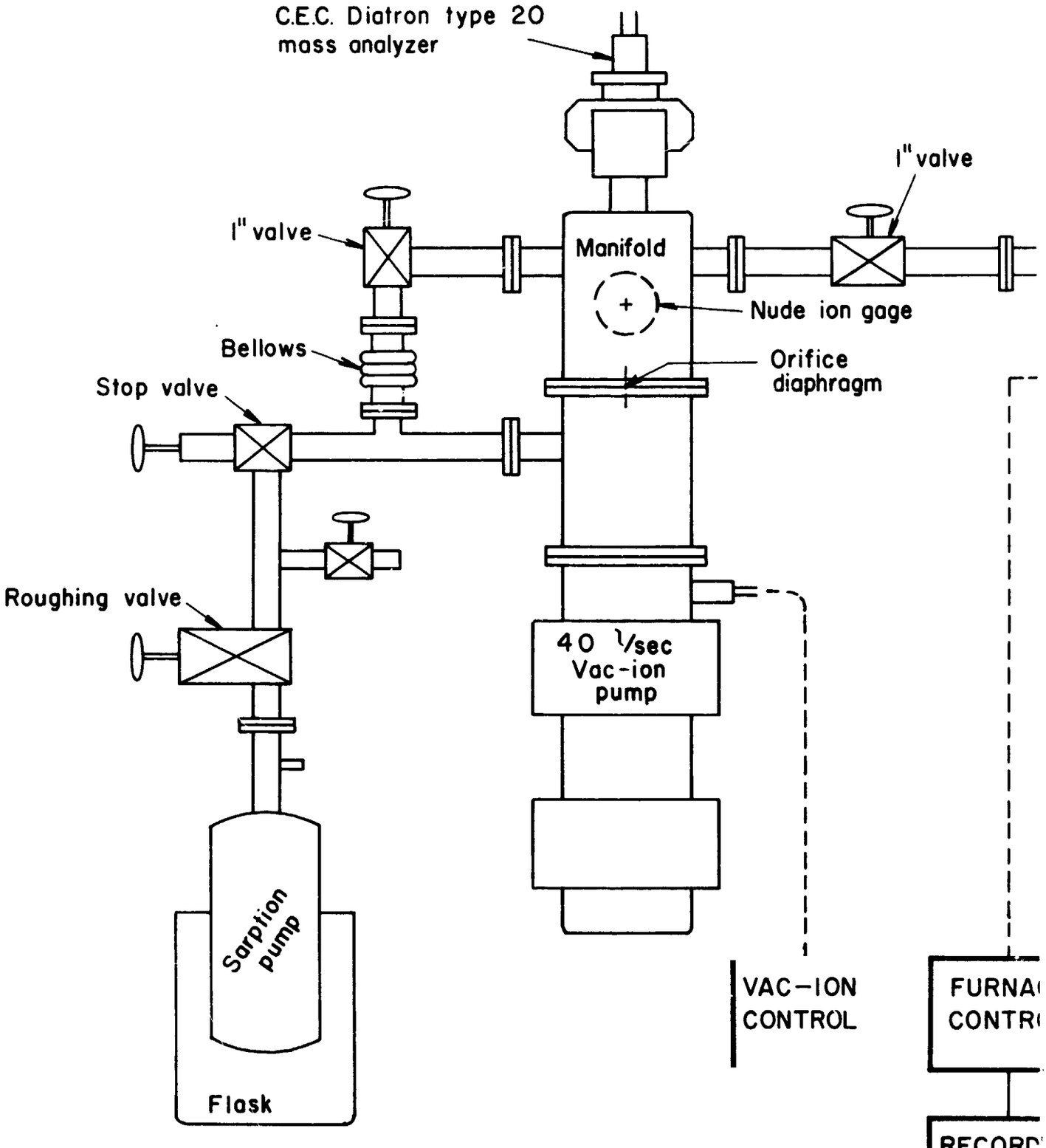
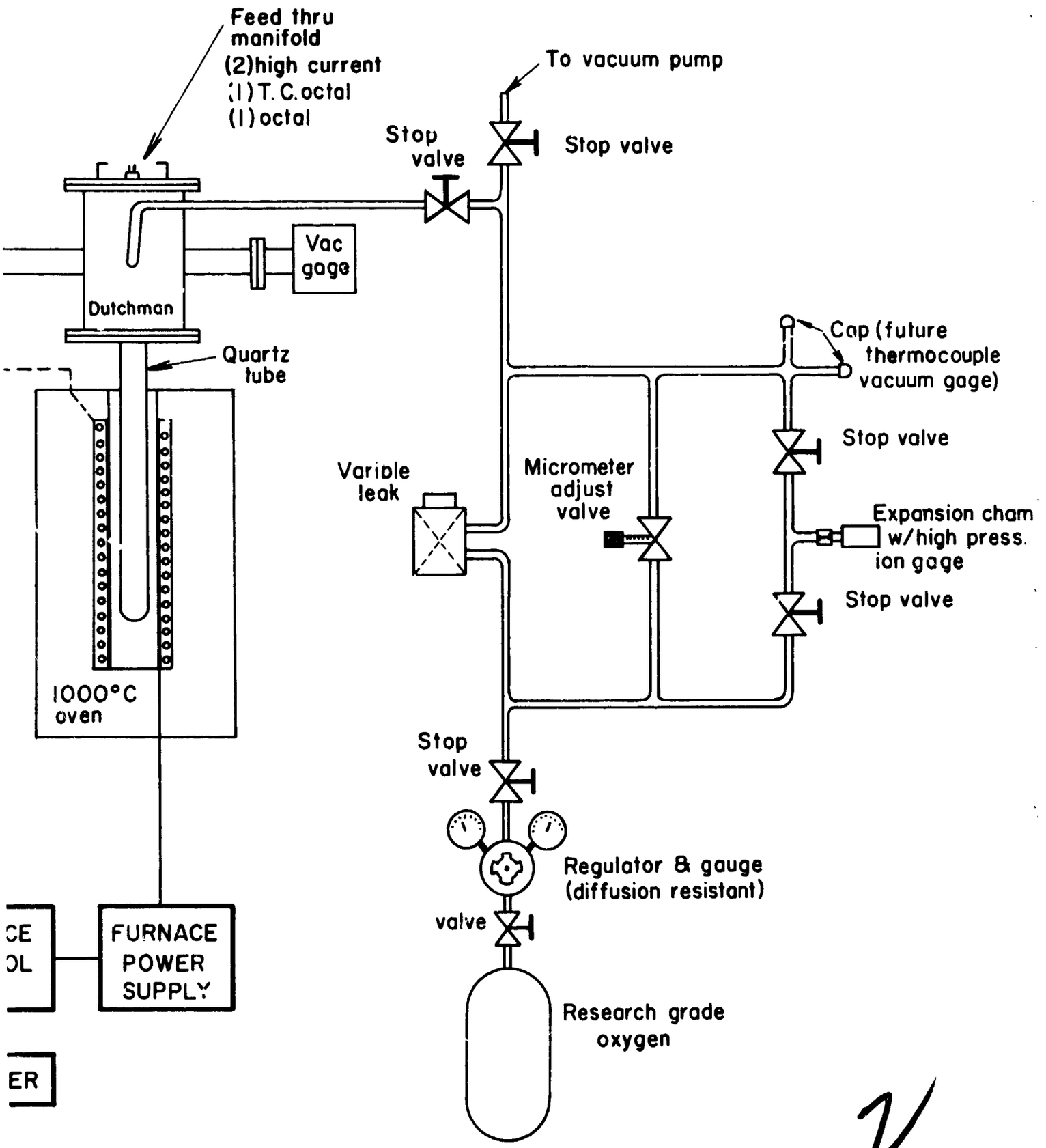


FIG. 2 PROFILE OF 1000°C FURNACE



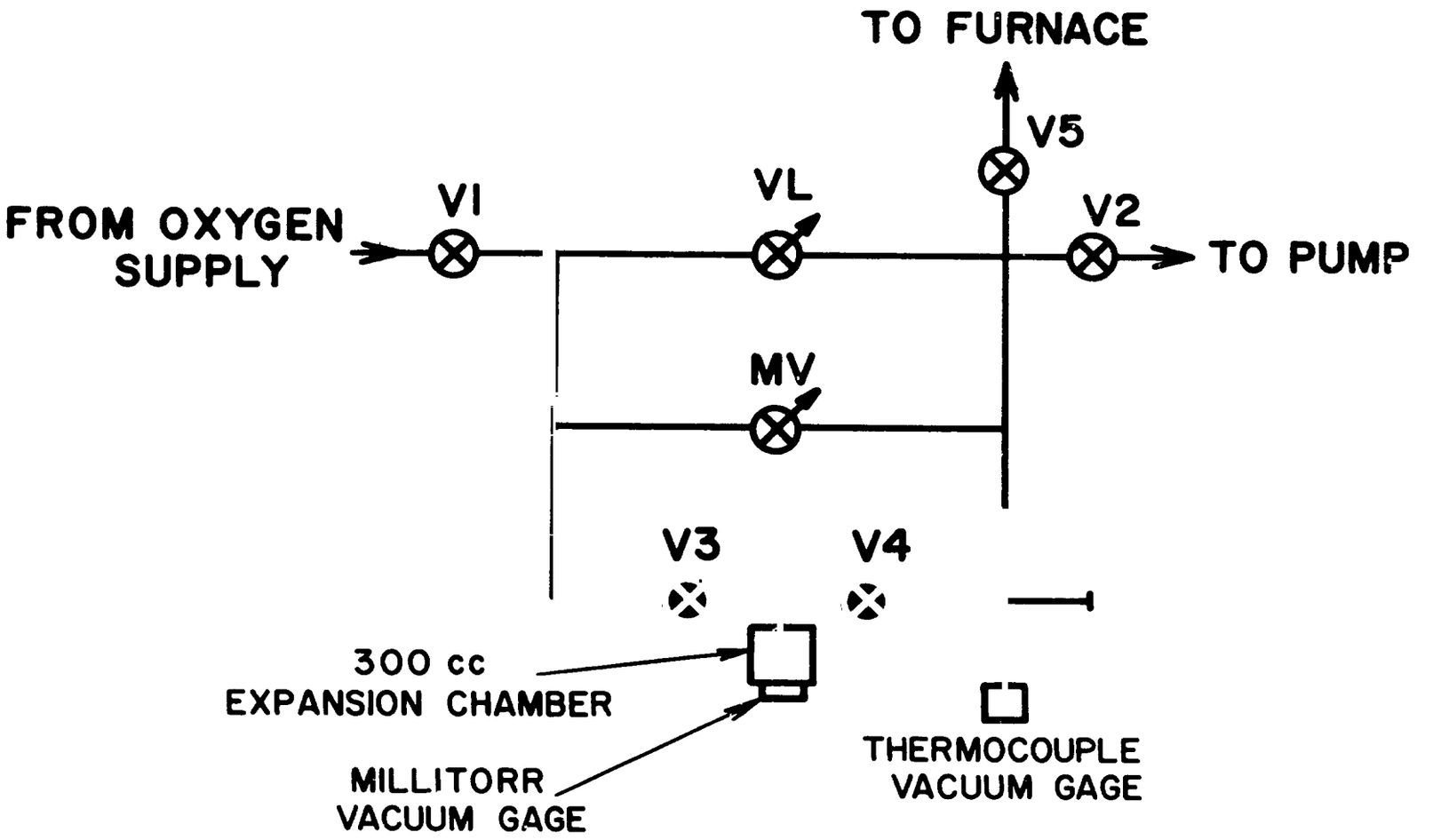
FUNCTIONAL BLO
FOR OXYGEN



V

:K DIAGRAM APPARATUS
SOLUBILITY STUDIES

Fig. 3



MV : Micrometer metering valve
VL : Granville - Phillips variable leak
V : High vacuum bakable valves

Fig. 4 OXYGEN FEED SYSTEM

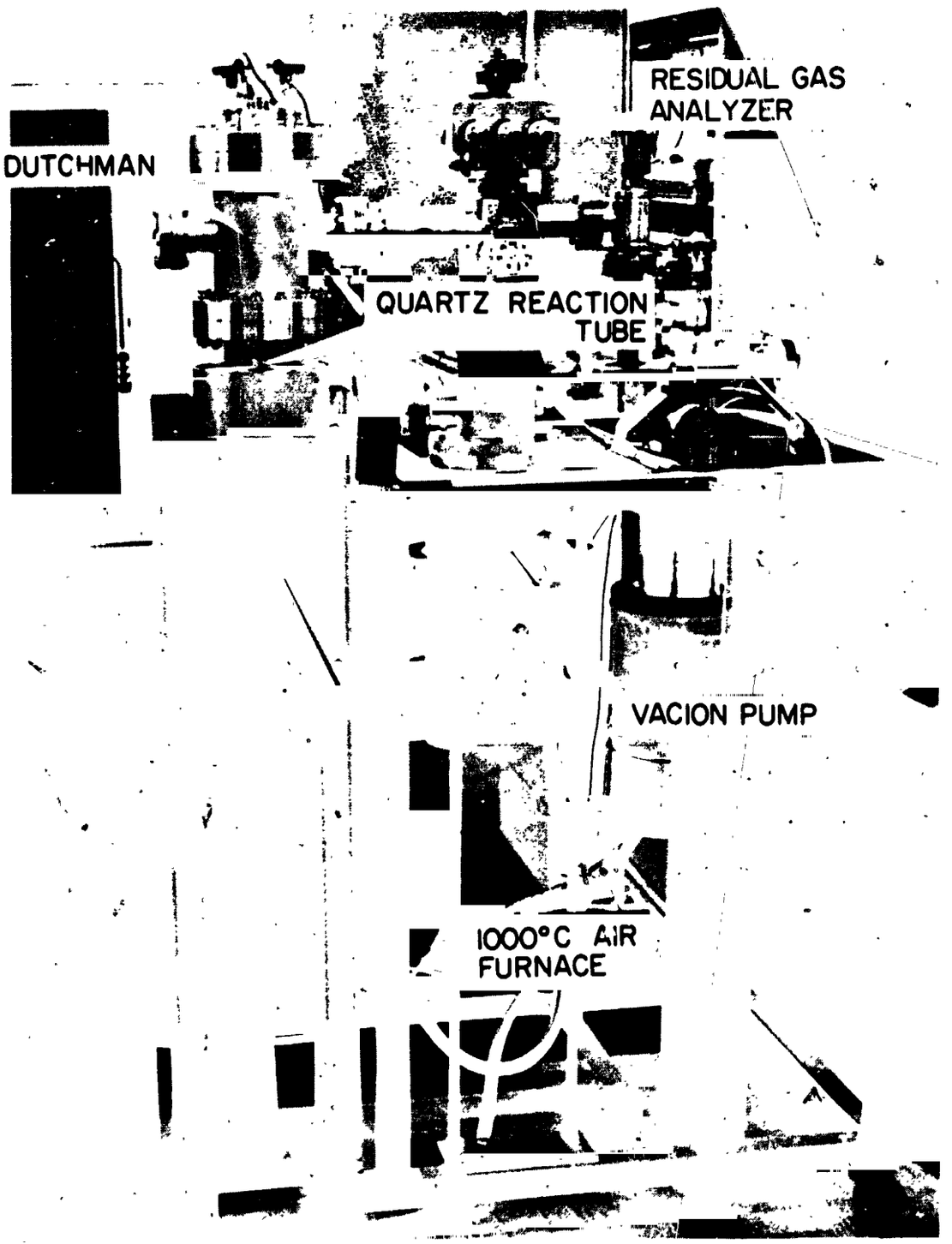


FIG. 5
REAR VIEW OF
SOLUBILITY APPARATUS
PHASE I

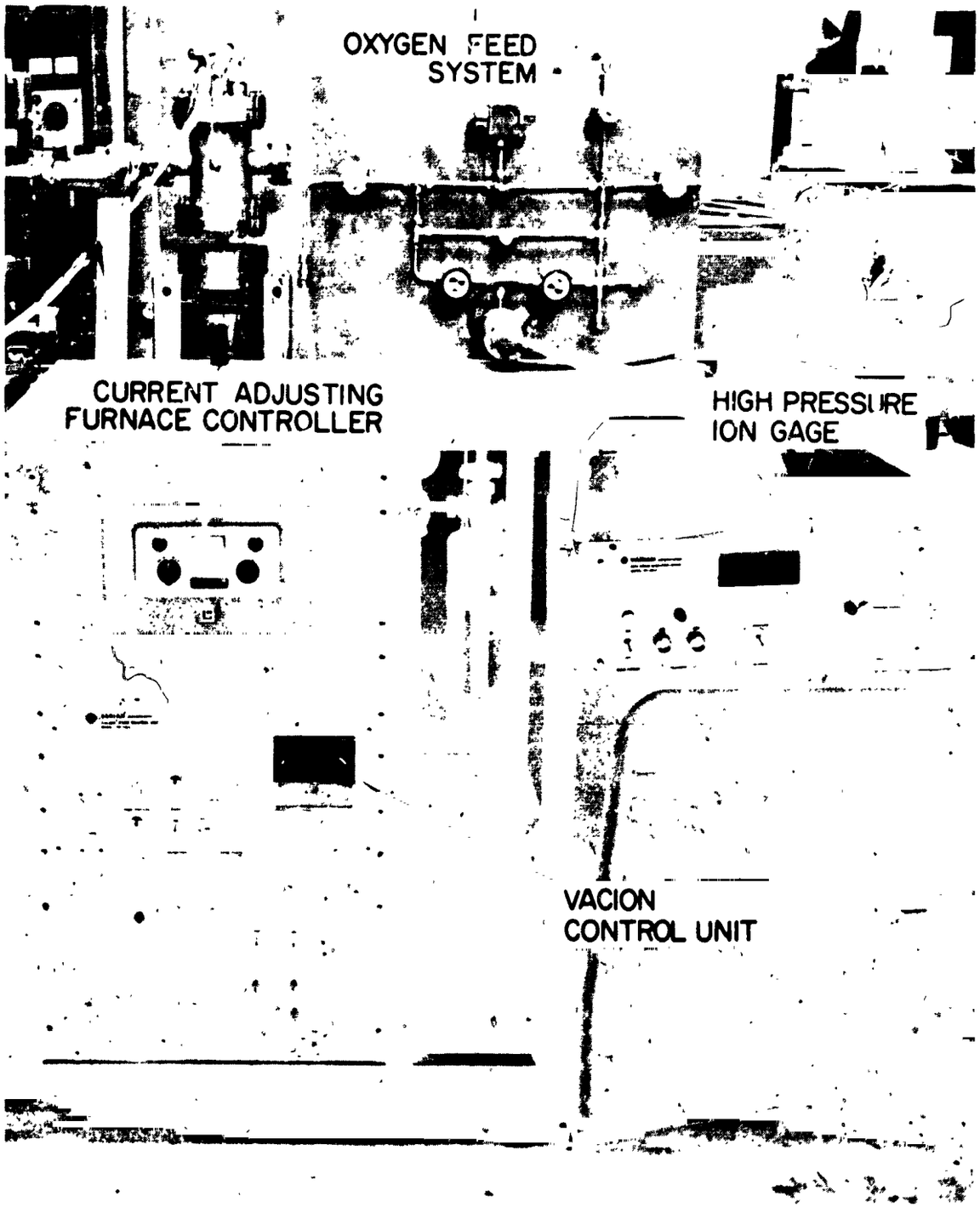


FIG. 6
FRONT VIEW OF
SOLUBILITY APPARATUS
PHASE I

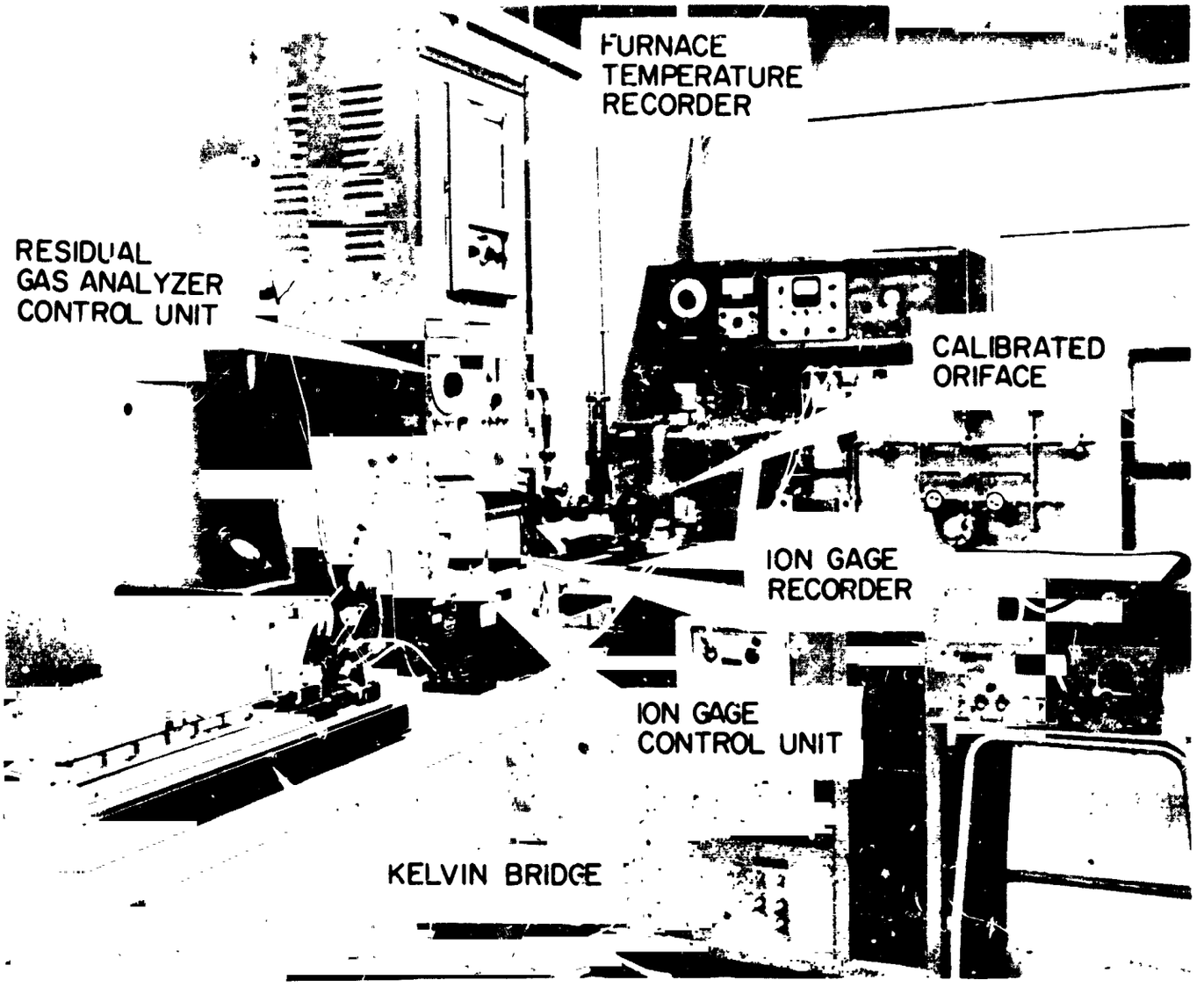


FIG. 7

OVERALL VIEW OF SOLUBILITY APPARATUS
PHASE I